

CHE 301 #2

Spring 2017

26-03-2017

Thermodynamic properties of fluids

• Property relations

$H \mid A \mid G$

System	Primary Properties P, V, T, U, S			
Homogeneous fluid with constant composition (closed system)	Internal energy, U	Enthalpy, H	Helmholtz energy, A	Gibbs energy, G
	$dU = dQ + dW$ $dU = TdS - PdV$	$dH = TdS + VdP$ $H = U + PV$	$dA = -PdV - SdT$ $A = U - TS$	$dG = VdP - SdT$ $G = H - TS$

• Maxwell relations

Exact differential equation of a function $F(x,y)$: $dF = \left(\frac{\partial F}{\partial x}\right)_y dx + \left(\frac{\partial F}{\partial y}\right)_x dy$ Total differential

$dF = M dx + N dy$ Criterion

Cross relations $\rightarrow \left(\frac{\partial M}{\partial y}\right) = \left(\frac{\partial N}{\partial x}\right)$

$dU = TdS - PdV$	$dH = TdS + VdP$	$dA = -PdV - SdT$	$dG = VdP - SdT$
$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$	$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

• Enthalpy and entropy as functions of T and P : $C_p dT + (1 - \beta T) V dP$

$H = H(T, P)$ Enthalpy	$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$
$S = S(T, P)$ Entropy	$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP = C_p \frac{dT}{T} - \left(\frac{\partial V}{\partial T}\right)_P dP$
$\left(\frac{\partial H}{\partial T}\right)_P = T \frac{\partial S}{\partial T} + 0 \quad ; \quad = C_p \frac{dT}{T} - \beta V dP$	

2.1.5(c) The variation of enthalpy with temperature

$$dH = C_p dT \quad (\text{at constant pressure})$$

$$\Delta H = C_p \Delta T \quad (\text{at constant pressure})$$

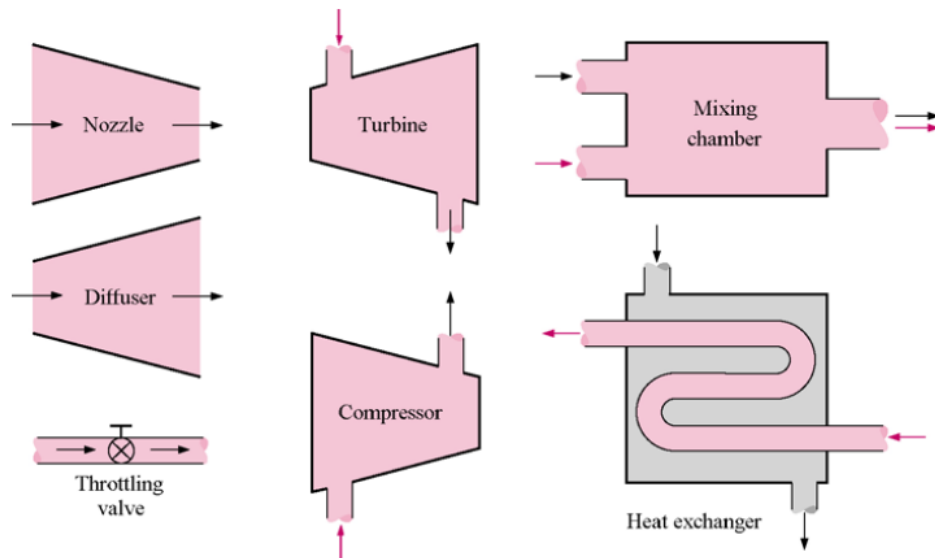
$$q_p = C_p \Delta T$$

$$C_{p,m} = a + bT + \frac{c}{T^2}$$

Table 2.2* Temperature variation of molar heat capacities, $C_{p,m}/(\text{J K}^{-1} \text{ mol}^{-1}) = a + bT + c/T^2$

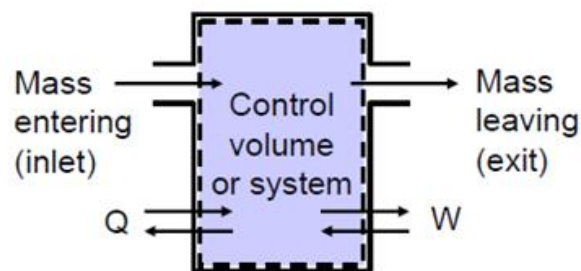
	a	$b/(10^{-3} \text{ K})$	$c/(10^5 \text{ K}^2)$
C(s, graphite)	16.86	4.77	-8.54
CO ₂ (g)	44.22	8.79	-8.62
H ₂ O(l)	75.29	0	0
N ₂ (g)	28.58	3.77	-0.50

Below are some engineering devices that operate essentially as steady-state, steady-flow control volumes.



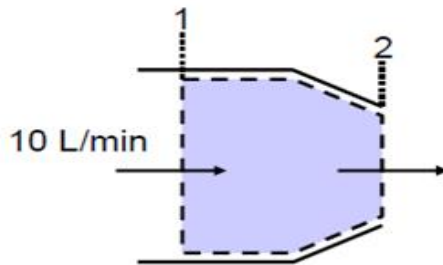
C. Conservation of Energy for an Open System

1. The law of conservation of energy can be applied to a control volume



$$\left(\text{Time rate of change of energy within control volume} \right) = \left(\text{net rate of energy crossing boundary as work and heat} \right) + \left(\text{total rate of energy entering CV with mass} \right) - \left(\text{total rate of energy exiting CV with mass} \right)$$

- c. Example - liquid water with a constant density of 1000 kg/m^3 enters a nozzle at the rate 10 L/min . The inlet of the nozzle has a diameter of 1.50 cm , the diameter of the exit is 0.75 cm . Find the velocities of the water at the inlet and exit.



Given: Area = πr^2
 $r_1 = 0.0075 \text{ m}$
 $r_2 = 0.00375 \text{ m}$
 $\rho = 1000 \text{ kg/m}^3$
Find: V_1 and V_2
Model: one-dimensional, steady flow

Analysis

Because we are at steady state,

$$\frac{dm_{cv}}{dt} = 0 = \dot{m}_1 - \dot{m}_2 \quad \text{or} \quad \dot{m}_1 = \dot{m}_2 = \dot{m}$$

From the inlet volumetric flow rate,

$$\dot{m} = \rho V_1 A_1 = \rho \dot{V} = 10 \frac{\text{L}}{\text{min}} \frac{1 \text{ min}}{60 \text{ s}} \frac{1 \text{ kg}}{1 \text{ L}} = 0.1667 \frac{\text{kg}}{\text{s}}$$

The inlet velocity is

$$V_1 = \frac{\dot{m}}{\rho A_1} = \frac{0.1667 \frac{\text{kg}}{\text{s}}}{1000 \frac{\text{kg}}{\text{m}^3} \pi (0.0075 \text{ m})^2} = 0.943 \frac{\text{m}}{\text{s}}$$

and the exit velocity is

$$V_2 = V_1 \frac{A_1}{A_2} = 0.943 \frac{\text{m}}{\text{s}} \left(\frac{1.5}{0.75} \right)^2 = 3.77 \frac{\text{m}}{\text{s}}$$

2.2.8 Standard enthalpies of formation

- **Key Points:** Standard enthalpies of formation are defined in terms of the reference states of elements.
- (a) The standard reaction enthalpy is expressed as the difference of the standard enthalpies of formation of products and reactants.
- (b) Computer modelling is used to estimate standard enthalpies of formation.

Enthalpy of chemical change (reaction)

Enthalpy of reaction is the heat released or absorbed as a result of a chemical reaction

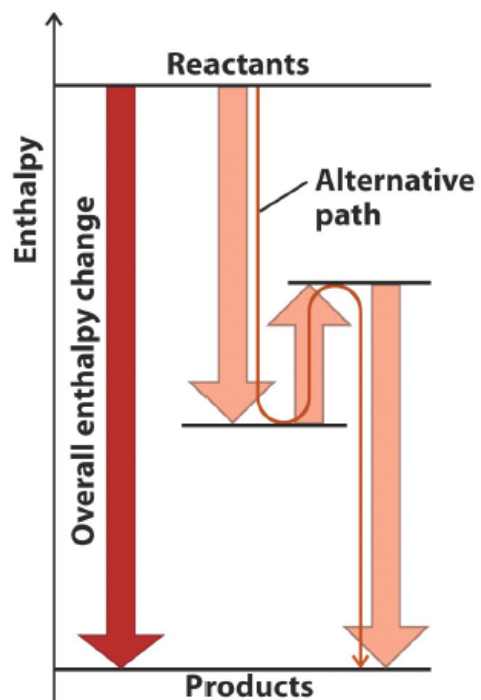
$$\Delta H_{\text{rxn}} = \sum H_{\text{products}} - \sum H_{\text{reactants}}$$

$$\Delta H_{\text{rxn}} = \Delta U_{\text{rxn}} + \Delta n_{\text{gas}}RT$$

Standard reaction enthalpy (ΔH°) refers to reactions where all products and reactants are in their standard state

Hess's law

The overall reaction enthalpy is the sum of the reaction enthalpies of the steps into which the reaction can be divided



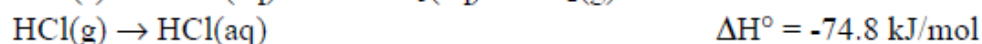
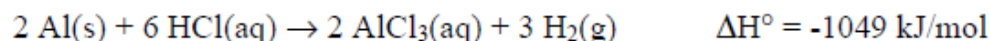
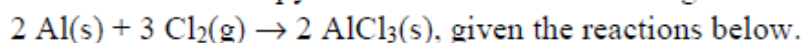
Hess' Law

Since enthalpy is a state function, we can choose more than one thermodynamic path to calculate a state function.

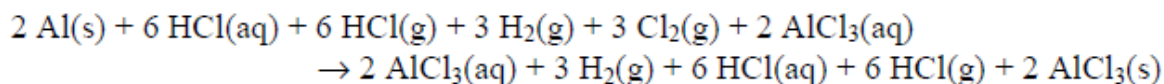
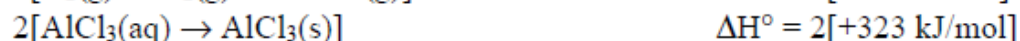
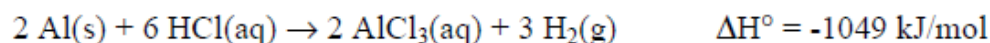
For chemical changes, Hess' Law states that the enthalpy of a reaction can be calculated from the enthalpies of all of the chemical step processes needed for the chemical reaction.

In other words, if reactions can be added together to form a resultant reaction, then enthalpies of the step reactions can be added to find a resultant enthalpy of reaction.

Example: Calculate the enthalpy of reaction for the following reaction:



Rearrange the equations such that their sum is the reaction of interest.



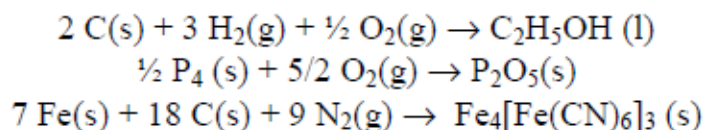
$$\begin{aligned} \Delta H^\circ &= -1049 \text{ kJ/mol} + 6[-74.8 \text{ kJ/mol}] + 3[-185 \text{ kJ/mol}] + 2[+323 \text{ kJ/mol}] \\ &= -1406 \text{ kJ/mol} \end{aligned}$$



Enthalpy of Formation

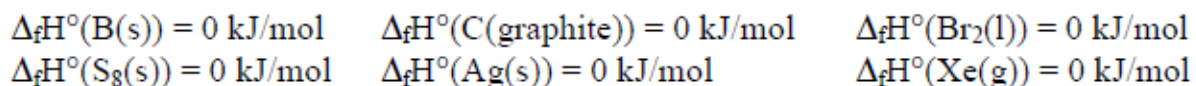
The enthalpy of formation is the enthalpy of a formation reaction for a particular substance.

A formation reaction is that where a compound is formed from elements in the naturally occurring state.



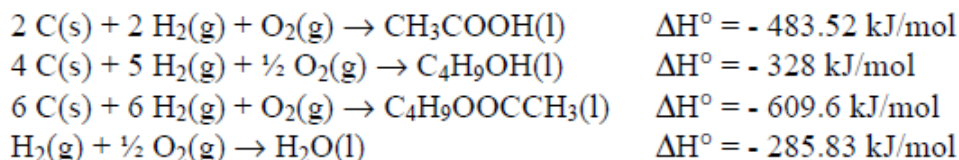
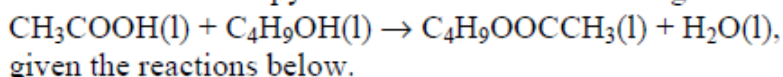
Enthalpy of formation of the elements

By definition, the enthalpy of formation of an element in its natural state is zero.



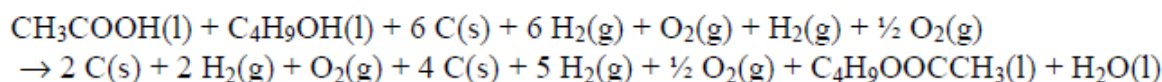
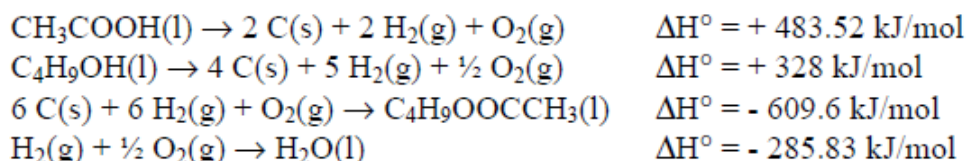
Reaction enthalpies can be calculated as a stoichiometric sum of enthalpies of formation. This technique is an application of Hess' law.

Example: Calculate the enthalpy of reaction for the following reaction:

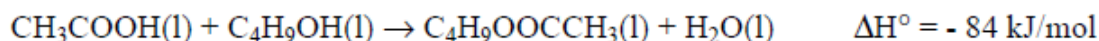


Note all of the above reactions are formation reactions.

Rearrange the equations such that their sum is the reaction of interest.



$$\Delta H^\circ = +483.52 \text{ kJ/mol} + 328 \text{ kJ/mol} - 609.6 \text{ kJ/mol} - 285.83 \text{ kJ/mol} = -84 \text{ kJ/mol}$$



Temperature Dependence of Internal Energy and Enthalpy

$$\text{Recall that } C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad \text{and} \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

These relationships imply that we can find the internal energy or enthalpy at a nonstandard temperature as long as we know the heat capacity.

$$dU = C_v dT \quad \text{and} \quad dH = C_p dT$$

Integrating both sides of these equations yields

$$\Delta U = \int C_v dT \quad \text{and} \quad \Delta H = \int C_p dT$$

For large temperature changes, we can't assume that the heat capacity is independent of temperature. Thus to calculate the internal energy or enthalpy at a nonzero temperature, we need the temperature dependence of the heat capacity.

Example: Calculate the change in enthalpy of $\text{H}_2(\text{g})$ from 373 K to 1000 K, given that the constant pressure heat capacity has the form $C_p = d + eT + fT^{-2}$ where $d = 27.28 \text{ J/K mol}$, $e = 0.00326 \text{ J/K}^2 \text{ mol}$ and $f = 0.00050 \text{ J K/mol}$.

$$\begin{aligned}\Delta H &= H_{1000\text{K}} - H_{373\text{K}} = \int C_p dT = \int (d + eT + fT^{-2}) dT = \int_{373}^{1000} d dT + \int_{373}^{1000} eT dT + \int_{373}^{1000} fT^{-2} dT \\ &= d T \Big|_{373}^{1000} + \frac{eT^2}{2} \Big|_{373}^{1000} - \frac{f}{T} \Big|_{373}^{1000} = d(1000 - 373) + \frac{e}{2}(1000^2 - 373^2) - 2f \left(\frac{1}{1000} - \frac{1}{373} \right) \\ &= (27.28 \text{ J/K} \cdot \text{mol})(627 \text{ K}) + \frac{0.00326 \text{ J/K}^2 \cdot \text{mol}}{2}(860871 \text{ K}^2) \\ &\quad - 2(0.00050 \text{ J} \cdot \text{K/mol})(-0.0016810 \text{ K}^{-1}) \\ &= 17105 \text{ J/mol} + 1403 \text{ J/mol} + 1.68 \times 10^{-6} \text{ J/mol} = 18508 \text{ J/mol} = 18.51 \text{ kJ/mol}\end{aligned}$$

Kirchoff's law

$$\Delta_r H(T) = \Delta_r H^0(298 \text{ K}) + \int_{298}^T \sum_i \nu_i C_{p,i} dT$$

That is by taking a stoichiometric sum of the heat capacities and integrating over the temperature range, we can find the correction to the reaction enthalpy at a non standard state temperature.

Example: 471 kJ/mol is the reaction enthalpy under standard conditions for the following reaction: $2 \text{Fe}_2\text{O}_3(\text{s}) + 3 \text{C}(\text{s}) \rightarrow 4 \text{Fe}(\text{s}) + 3 \text{CO}_2(\text{g})$. What is the reaction enthalpy at 1000 K?

According to the NIST Webbook Internet site, the constant pressure heat capacities of the chemical species in the above smelting process can be fitted according to the Shumate equation, $C_p = A + B T + C T^2 + D T^3 + E T^{-2}$

The values for A, B, C, D and E for each species are given below.

	A	B	C	D	E
Fe_2O_3	93.43834	0.108358	-5.08645×10^{-5}	2.56×10^{-8}	-1610000
C	10.68	0	0	0	0
CO_2	24.99735	0.055187	-3.36914×10^{-5}	7.95×10^{-9}	-137000
Fe	18.42868	0.024643	-8.91×10^{-6}	9.66×10^{-9}	-12600
Sum	-70.2099	0.047418	-3.50×10^{-5}	1.13×10^{-8}	2762174

$$\Delta_r H(1000 \text{ K}) = \Delta_r H^0(298 \text{ K}) + \int_{298 \text{ K}}^{1000 \text{ K}} \sum_i \nu_i (A_i + B_i T + C_i T^2 + D_i T^3 + E_i T^{-2}) dT$$

$$= \Delta_r H^0(298 \text{ K}) + \sum_i \nu_i \left(A_i T \Big|_{298}^{1000} + \frac{B_i}{2} T^2 \Big|_{298}^{1000} + \frac{C_i}{3} T^3 \Big|_{298}^{1000} + \frac{D_i}{4} T^4 \Big|_{298}^{1000} - E_i T^{-1} \Big|_{298}^{1000} \right)$$

$$\Delta_r H(1000 \text{ K}) = \frac{471 \text{ kJ}}{\text{mol}} + (-70.2099)(1000 - 298) + \frac{(0.047418)}{2}(1000^2 - 298^2)$$

$$+ \frac{(-3.50 \times 10^{-5})}{3}(1000^3 - 298^3) + \frac{(1.13 \times 10^{-8})}{4}(1000^4 - 298^4) - 2762174 \left(\frac{1}{1000} - \frac{1}{298} \right)$$

$$\Delta_r H(1000 \text{ K}) = \frac{471 \text{ kJ}}{\text{mol}} - \frac{49.3 \text{ kJ}}{\text{mol}} + \frac{21.6 \text{ kJ}}{\text{mol}} - \frac{34.1 \text{ kJ}}{\text{mol}} + \frac{11.2 \text{ kJ}}{\text{mol}} - \frac{6.5 \text{ kJ}}{\text{mol}} = \frac{413.9 \text{ kJ}}{\text{mol}}$$

Kirchoff's Law can be stated with in a differential form as well.

$$\text{Include} \left(\frac{\partial \Delta U}{\partial T} \right)_V = \Delta C_V \quad \text{and} \quad \left(\frac{\partial \Delta H}{\partial T} \right)_P = \Delta C_P$$

specific enthalpy, the enthalpy of combustion per gram of material. If the standard enthalpy of combustion is $\Delta_c H^\circ$ and the molar mass of the compound is M , then the specific enthalpy is $\Delta_c H^\circ/M$

Table 2.6* Standard enthalpies of formation and combustion of organic compounds at 298 K

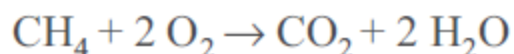
	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_c H^\circ/(\text{kJ mol}^{-1})$
Benzene, $\text{C}_6\text{H}_6(\text{l})$	+49.0	−3268
Ethane, $\text{C}_2\text{H}_6(\text{g})$	−84.7	−1560
Glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$	−1274	−2808
Methane, $\text{CH}_4(\text{g})$	−74.8	−890
Methanol, $\text{CH}_3\text{OH}(\text{l})$	−238.7	−726

Table 2.5 Thermodynamic data for organic compounds (all values are for 298 K)

	$M/(\text{g mol}^{-1})$	$\Delta_f H^\circ/(\text{kJ mol}^{-1})$	$\Delta_f G^\circ/(\text{kJ mol}^{-1})$	$S_m^\circ/(\text{J K}^{-1} \text{mol}^{-1})^\dagger$	$C_{p,m}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$	$\Delta_c H^\circ/(\text{kJ mol}^{-1})$
C(s) (graphite)	12.011	0	0	5.740	8.527	−393.51
C(s) (diamond)	12.011	+1.895	+2.900	2.377	6.113	−395.40
$\text{CO}_2(\text{g})$	44.040	−393.51	−394.36	213.74	37.11	
Hydrocarbons						
$\text{CH}_4(\text{g})$, methane	16.04	−74.81	−50.72	186.26	35.31	−890
$\text{CH}_3(\text{g})$, methyl	15.04	+145.69	+147.92	194.2	38.70	
$\text{C}_2\text{H}_2(\text{g})$, ethyne	26.04	+226.73	+209.20	200.94	43.93	−1300
$\text{C}_2\text{H}_4(\text{g})$, ethene	28.05	+52.26	+68.15	219.56	43.56	−1411
$\text{C}_2\text{H}_6(\text{g})$, ethane	30.07	−84.68	−32.82	229.60	52.63	−1560
$\text{C}_3\text{H}_6(\text{g})$, propene	42.08	+20.42	+62.78	267.05	63.89	−2058
$\text{C}_3\text{H}_6(\text{g})$, cyclopropane	42.08	+53.30	+104.45	237.55	55.94	−2091
$\text{C}_3\text{H}_8(\text{g})$, propane	44.10	−103.85	−23.49	269.91	73.5	−2220
$\text{C}_4\text{H}_8(\text{g})$, 1-butene	56.11	−0.13	+71.39	305.71	85.65	−2717
$\text{C}_4\text{H}_8(\text{g})$, <i>cis</i> -2-butene	56.11	−6.99	+65.95	300.94	78.91	−2710
$\text{C}_4\text{H}_8(\text{g})$, <i>trans</i> -2-butene	56.11	−11.17	+63.06	296.59	87.82	−2707
$\text{C}_4\text{H}_{10}(\text{g})$, butane	58.13	−126.15	−17.03	310.23	97.45	−2878
$\text{C}_5\text{H}_{12}(\text{g})$, pentane	72.15	−146.44	−8.20	348.40	120.2	−3537
$\text{C}_5\text{H}_{12}(\text{l})$	72.15	−173.1				
$\text{C}_6\text{H}_6(\text{l})$, benzene	78.12	+49.0	+124.3	173.3	136.1	−3268

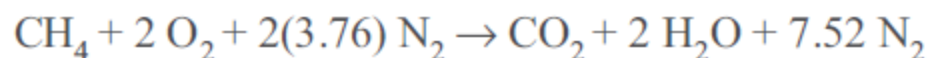
COMBUSTION PROCESSES

First, the combustion equation should be written and balanced. For example, for the stoichiometric combustion of methane in oxygen:



Combustion in Air

For each mole of oxygen, there will be 3.76 moles of nitrogen. For stoichiometric combustion of methane in air:



Combustion in Excess Air

The excess oxygen appears as oxygen on the right side of the combustion equation.

Table 2.7 Thermochemical properties of some fuels

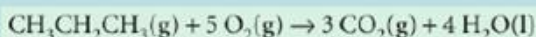
Fuel	Combustion equation	$\Delta_c H^\circ /$ (kJ mol ⁻¹)	Specific enthalpy/ (kJ g ⁻¹)	Enthalpy density/ (kJ dm ⁻³)
Hydrogen	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-286	142	13
Methane	$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-890	55	40
Octane	$\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2} \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{l})$	-5471	48	3.8×10^4
Methanol	$\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-726	23	1.8×10^4

Example 2.5 Using Hess's law

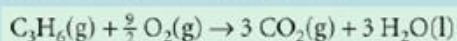
- The standard reaction enthalpy for the hydrogenation of propene,



- is -124 kJ mol^{-1} . The standard reaction enthalpy for the combustion of propane,



- is $-2220 \text{ kJ mol}^{-1}$. Calculate the standard enthalpy of combustion of propene.
- Answer** The combustion reaction we require is



- This reaction can be recreated from the following sum:

	$\Delta_r H^\circ / (\text{kJ mol}^{-1})$
$\text{C}_3\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$	-124
$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$	-2220
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$	$+286$
$\text{C}_3\text{H}_6(\text{g}) + \frac{9}{2} \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$	-2058

- Test 2.6** Calculate the enthalpy of hydrogenation of benzene from its enthalpy of combustion and the enthalpy of combustion of cyclohexane.
- Correct Answer:** -205 kJ mol^{-1}

Table 2.7 Thermochemical properties of some fuels

Fuel	Combustion equation	$\Delta_c H^\circ / (\text{kJ mol}^{-1})$	Specific enthalpy / (kJ g^{-1})	Enthalpy density / (kJ dm^{-3})
Hydrogen	$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$	-286	142	13
Methane	$\text{CH}_4(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-890	55	40
Octane	$\text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2} \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{l})$	-5471	48	3.8×10^4
Methanol	$\text{CH}_3\text{OH}(\text{l}) + \frac{3}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	-726	23	1.8×10^4